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<b>(21) International Application Number:</b> PCT/US97/05630 <b>(22) International Filing Date:</b> 3 April 1997 (03.04.97)  <b>(30) Priority Data:</b> 60/014,808                      4 April 1996 (04.04.96)                      US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventors:</b> GREY, Ronald, L.; 109 Dyer Avenue, New Castle, DE 19720 (US). ZUFFEREY, Prosper; 72, chemin Saule, CH-1233 Bemex (CH).  <b>(74) Agent:</b> EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> BR, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> INJECTION MOLDING PROCESS  <b>(57) Abstract</b>  A process for making injection molded articles particularly ones having swirl patterns of polyamide in an ionomer (marble effect) employing a reciprocating screw injection molding machine is provided. The process involves making a nylon/colorant master batch and using a reciprocating screw injection machine to mold the nylon/colorant master batch and an ionomer under conditions that maintain the nylon/colorant master batch in a state wherein it will flow but will have a viscosity greater than the ionomer so that it will not disperse well in the ionomer at the temperature of injection molding.		

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**TITLE**  
**INJECTION MOLDING PROCESS**

**FIELD OF THE INVENTION**

5           This invention relates to a process for creating a injection molded articles particularly ones having swirl patterns of polyamide in an ionomer (marble effect) employing a reciprocating screw injection molding machine. Such articles have particular utility in designer containers for cosmetics, caps for perfume bottles, and other decorative items.

**BACKGROUND OF THE INVENTION**

10           Use of ionomers such as SURLYN® ionomer available from E. I. du Pont de Nemours and Company, for making a wide variety of molded parts is well known. Such molded parts generally are uniform in color. Some variations in color can be obtained using plunger-type molding machines. In this type machine, the plastic pellets are delivered into the machine hopper from which  
15           they are volumetrically dropped into the heated cylinder while the ram is retracted. At the beginning of the injection cycle, the ram pushes rapidly forward and forces the resin into the cylinder, compacting it tightly behind and around the centrally located plasticizing torpedo or spreader. Fins center the torpedo and transfer heat to it from the cylinder walls. Heat and pressure join in plasticizing  
20           the resin. As the melt moves forward into the injection chamber of the cylinder, it reaches the required temperature and fluidity for injection through the cylinder nozzle into the mold cavity by the sustained forward motion of the plunger.

          The properties of certain ionomers, particularly optical clarity, have established the ionomers as the material of choice in the European Cosmetic  
25           Industry for making perfume bottle caps, mostly in a clear or transparent color state, for women fragrances. There is a growing demand from perfume companies & their designers, for other looks. One such look that is desired is a swirled pattern, that is diffusive coloration with colored veins, ("marble effect"). Another desired appearance is that in which colored swirls appear as floating in a  
30           clear or tinted outer material ("cats eye glass marble effect").

          Achieving such non-uniform colorations employing standard reciprocating screw injection molding machines is desired. In a reciprocating-screw injection molding machine, a rotating screw, similar to those used in extruders replaces the plunger. Usually, the rotating screw first moves the  
35           melting resin forward and then is itself forced backward by the accumulated melt until the volume of melt required for an injection shot has accumulated in front of

the tip of the screw. Then the screw normally stops turning, rapidly moves forward, and ramlike, pushes the melt through the nozzle into the mold.

### **SUMMARY OF THE INVENTION**

5                   A process has now been found that achieves the marble effect, preferably in a single injection process, and the cats eye glass marble effect, preferably in a co-injection process, using reciprocating screw injection molding machines.

10                  The single injection process comprises injection molding in a salt and pepper blend of ionomer and nylon in a single injection machine, that is an injection molding machine characterized as one having a single barrel through which resin is shot into the nozzle feeding the sprues and gates into the mold.

15                  The co-injection process comprises injection molding the ionomer and nylon in a co-injection machine, that is an injection molding machine characterized as one having more than one barrel, preferably two, through which resin is shot into the nozzle feeding the sprues and gates into the mold. The co-injection process differs from the single injection process in that a salt and pepper blend on the ionomer and nylon is not made. Instead, the desired quantity of ionomer is introduced through one barrel into the nozzle and the desired quantity  
20                  of nylon is then introduced through another barrel into the nozzle prior to being fed to the sprues and gates into the mold.

                  The selection of the ionomer, the nylon, and additives such as colorants as well as the conditions employed in the injection process are important for achieving the desired effects.

25                  The ionomer may be selected from copolymers of ethylene and  $\alpha$ ,  $\beta$ -ethylenically-unsaturated  $C_3$ -  $C_8$  carboxylic acid (preferably acrylic acid or methacrylic acid) partially neutralized with monovalent and/or bivalent metal cations, preferably sodium, lithium, or magnesium, more preferably sodium.

                  The nylon must be carefully selected so that at processing  
30                  temperature it will flow but not disperse well in the ionomer. Theoretically, one could accomplish this by controlling the viscosities of the materials by selecting a nylon having a higher melting point than the ionomer and operating at a processing temperature above that of the ionomer melting point but just below that of the nylon. If one operates too far above the melting point of the ionomer,  
35                  however, degradation of the ionomer will occur. Therefore, the nylon should be one that has a softening point that is not significantly higher than that of the ionomer particularly if non-yellowed, optically clear ionomer is desired.

The ionomer may be clear or tinted if a background color is desired. The nylon likewise may be colored, preferably with a colorant that differs from that used in the ionomer.

5 Semicrystalline polyamides, particularly polyepsilon-caprolactam (nylon-6) which has a melting point close to that of the ionomer, can be used. Amorphous polyamides, particularly those blended with ethylene vinyl alcohol available from E. I. du Pont de Nemours and Company under the tradename SELAR®PA, are preferred since they soften but do not melt at temperatures close to that of the ionomer.

10 Tighter operating conditions are needed with nylon 6, which has a relatively sharp melting point of 205 °C. If the ionomer/nylon blend is melt extruded above the nylon melting point that the nylon will become quite fluid and disperse too well in the ionomer resulting in no marble effect. At temperatures less than 200 °C, unmelted, not esthetically pleasing, nylon could be seen in the  
15 part. At 205 °C, large swirls of color, close to those of a natural marble, result. Additionally, gate size and location are critical. With amorphous nylon a much broader processing window exists.

#### **DETAILED DESCRIPTION OF THE INVENTION**

The single injection process of the present invention comprises  
20 first making a salt and pepper blend of a nylon/colorant master batch and an ionomer, which can optionally also be blended with colorant, preferably different from that used in the nylon/colorant master batch. The salt and pepper blend is then injection molded using a reciprocating screw injection machine, preferably one having a single barrel, under conditions that maintain the nylon/colorant  
25 master batch in a state wherein it will flow but will have a viscosity greater than the ionomer so that it will not disperse well in the ionomer at the temperature of injection. The barrel feeds a nozzle which in turn feeds one or more sprues and, in turn, gates in the mold. The gates are positioned so to impinge on the wall of the cavity or the core in the cavity.

30 The co-injection process of the present invention comprises first feeding the ionomer through one or more than one barrel connected to a nozzle followed closely by feeding the nylon/colorant blend through another barrel connected the same nozzle. For each additional component desired (for example, another nylon/colorant), another barrel can be used. As in the case of the single  
35 injection process, the reciprocating screw injection machine should be operated under conditions that maintain the nylon/colorant master batch in a state wherein it will flow but will have a viscosity greater than the ionomer so that it will not disperse well in the ionomer at the temperature of injection. The barrels feed a

nozzle which in turn feeds one or more sprues and, in turn, gates in the mold. The gates are positioned so to impinge on the wall of the cavity or the core in the cavity.

5 The temperature in each case should be close to the melting point of the ionomer to avoid discoloration that comes if too high a temperature is used and residence time in the extruder should be kept short for production economies and to avoid prolonged exposure to elevated temperatures that will degrade the ionomer. For semicrystalline nylons, tight control of operating conditions is needed. The temperature of process must be controlled above the melting point  
10 of the ionomer and no higher than the melting point of the nylon but no lower than a temperature about 5°C below the melting point of the nylon. One skilled in the art will be able to select an operating temperature based on the teachings herein to assure that the semicrystalline nylon flows (does not have unmelted, non-esthetically pleasing pieces in the finished piece) but is not so fluid that it  
15 fully disperses in the ionomer. For nylon 6, the temperature should be greater than 200 °C but less than 205°C, more preferably from about 203°C to about 205°C.

For amorphous nylon, the temperature range that can be employed is much broader, however, since the amorphous nylon has a softening  
20 point and not a sharp melting point. The temperature should be sufficiently high to melt the ionomer and soften the nylon. The temperature should also be close to the melting point of the ionomer and the residence time in the extruder should be kept short for production economies and to avoid prolonged exposure to elevated temperatures that will degrade the ionomer. Preferred operating  
25 temperatures are about 350 °F to about 480 °F.

The injection machine should be operated in a manner that minimizes mixing of the nylon/colorant master batch and the ionomer, that is the screw should be operated at a slow screw speed, albeit one that is high enough to assure that the screw can fully return to its starting position in time for enough  
30 resin for each subsequent shot. Preferably screw speeds of about 20 to 25 revolutions per minute should be used. The extruder should preferably be operated with the shot size being close to maximum so that the material in front of the screw does not experience repeated mixing with each screw rotation. Back pressure on the extruder should be low, preferably no more than 25 pounds  
35 per square inch.

The gate through which the material is injected into the mold should be small and positioned so that the injected material impinges of the cavity wall or core of the mold. For semicrystalline nylon, the gate size must be very

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small, preferably 0.020 to about 0.050 inches in diameter, more preferably 0.020 to about 0.040 inches. For amorphous nylon, the gate size is not critical and can preferably be from about 0.020 to about 0.100 inches in diameter, preferably about 0.020 to about 0.050 inches.

- 5 About 0.5 to about 40 weight percent nylon/colorant master batch based on weight of the ionomer can be used. Preferably the nylon/colorant master batch is about 1 to 5 weight percent of the ionomer for best clarity and good swirl pattern. As the percent nylon is increased, clarity decreases. At about 30 to about 40 weight percent, excellent swirl pattern can be achieved, but  
10 the clarity is low.

The components of the present invention are as follows:

### Nylon

- Semicrystalline polyamides can be used in the present invention. Preferably they should have a sufficiently low (close to that of the ionomer)  
15 melting point. The term "semicrystalline polyamide" is well known to those skilled in the art. Semicrystalline polyamides suitable for this invention are generally prepared from lactams or amino acids or from condensation of diamines such as hexamethylene diamine with dibasic acids such as sebacic acid. Copolymers and terpolymers of these polyamides are also included.  
20 Polyepsiloncaprolactam (nylon-6) is particularly preferred because of its low melting point, about 205 °C.

- Amorphous polyamides can be substituted for some or all of the semicrystalline polyamide. The term "amorphous polyamide" is well known to those skilled in the art. "Amorphous polyamide," as used herein, refers to those  
25 polyamides which are lacking in crystallinity as shown by the lack of an endotherm crystalline melting peak in a Differential Scanning Calorimeter ("DSC") measurement (ASTM D-3417), 10°C./minute.

- Examples of the amorphous polyamides that can be used include those amorphous polymers prepared from the following diamines:  
30 hexamethylenediamine, 2-methylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, bis(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)isopropylidene, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, meta-xylylenediamine, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethyldiaminobutane,  
35 1,4-diaminomethylcyclohexane, p-xylylenediamine, m-phenylenediamine, p-phenylenediamine, and alkyl substituted m-phenylenediamine and p-phenylenediamine.

Examples of polyamides that can be used include those amorphous polymers prepared from the following diacarboxylic acids: isophthalic acid, terephthalic acid, alkyl substituted iso- and terephthalic acid, adipic acid, sebacic acid, butane dicarboxylic acid, and the like.

5           Specific examples of amorphous polyamides which are suitable for this invention include: hexamethylenediamine isophthalamide, hexamethylenediamine isophthalamide/terephthalamide terpolymer, having iso/-terephthalic moiety ratios of 100/0 to 60/40, mixtures of 2,2,4- and 2,4,4-trimethylhexamethylenediamine terephthalamide, copolymers of hexamethylene  
10   diamine and 2-methylpentamethylenediamine with iso-or terephthalic acids, or mixtures of these acids. Polyamides based on hexamethylenediamine iso/terephthalamide containing high levels of terephthalic acid moiety may also be useful provided a second diamine such as 2-methyldiaminopentane is incorporated to produce a processible amorphous polymer.

15           The above amorphous polyamides may contain as comonomers minor amounts of lactam species such as caprolactam or lauryl lactam, even though polymers based on these monomers alone are not amorphous. The important feature is that the polyamide as a whole must be amorphous. Thus small amounts of these comonomers may be incorporated as long as they do not  
20   impart crystallinity to the polyamide. In addition, up to about 10 weight % of a liquid or solid plasticizer such as glycerol, sorbitol, mannitol, or aromatic sulfonamide compounds (such as "Santicizer 8" from Monsanto) may be included with the amorphous polyamide.

          Preferably the amorphous polyamide is a blend of ethylene vinyl  
25   alcohol and amorphous nylon available from E. I. du Pont de Nemours and Company under the tradename SELAR®PA. The polyamide component comprises about 5 to about 95 percent by weight of the total composition of EVOH plus polyamide, preferably about 15 to about 70 percent, and most preferably about 15 to about 30 percent.

### 30   **Ionomer**

          The copolymers of ethylene and  $\alpha,\beta$ -ethylenically-unsaturated C<sub>3</sub>-C<sub>8</sub> carboxylic acid ("ethylene-acid copolymers") used to make the ionomeric copolymer of this invention have the acid moiety present in an amount of 10 to about 25, (preferably 12 to 16 or preferably 19 to 22) wt.% of the copolymer.  
35   The preferred acid moieties are methacrylic acid and acrylic acid.

          The ethylene-acid copolymers used to make the ionomeric copolymer can also be E/X/Y copolymers where E is ethylene; X is a softening comonomer and Y is the  $\alpha,\beta$ -ethylenically-unsaturated C<sub>3</sub>-C<sub>8</sub> carboxylic acid,



particularly acrylic or methacrylic acid. By "softening", it is meant that the polymer is made less crystalline. Suitable "softening comonomers (X) are monomers selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1 - 12 carbon atoms which, when present, may be up to 25  
5 (preferably up to 15, most preferably up to 10) wt.% of the ethylene-acid copolymer.

Specific ethylene-acid copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl  
10 acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate.

15 The acid moiety is partially neutralized with monovalent and/or bivalent metal cations such as lithium\*, sodium\*, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum (\*= preferred), or a combination of such cations. The mole percent of acid neutralized is up to about 70%, preferably 30 to 50%.

20 Ionomers can be made by processes well known in the art (see U.S. Pat. No. 3,262,272 to Rees, for example, which is incorporated herein by reference).

### **Method of Preparing Master Batches**

Colorants are blended with the nylon or ionomer, as the case may  
25 be, using known technology for obtaining good mixing. A twin screw extruder, for example, is a preferred melt mixing device. The color added preferably is about 1 to about 4 weight percent of the nylon or ionomer. Preferably the color added is a pigment that is non-bleeding, that is once it has been fully compounded with one component, it will not bleed into the other when the nylon and ionomer  
30 are melt blended during the injection molding process.

### **EXAMPLE**

#### **Examples 1**

A nylon 6/colorant master batch produced on a lab extruder at Plasti-Couleur, a French MB supplier. A white pigment (0.25 weight percent)  
35 and a black pigment (0.25 weight percent) were used to make the master batch.

In order to achieve the marble effect, SURLYN® ionomer PC100, a sodium neutralized 15% methacrylic acid ionomer available from E. I.

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du Pont de Nemours and Company mixed with 0.05 weight percent BASF "Sicoversal 23074 (wax based) was used.

5 The nylon and ionomer components were mixed and fed to a desk clock body tool having a sub-marine pin point gate located mid height of the clock back side placed on a Nestal 150 tons clamping molding machine, with a standard Nestal screw having a diameter of 40 mm. The resulting molded piece had a white marble appearance.

## Examples 2

10 Nylon master batch samples were made in a 30 mm twin screw extruder with 1% by weight of White Pearl color concentrate in the nylon. The master batches were tumble blended with Surlyn® PC-100 at master batch levels of 0.5% to 40% into a salt and pepper blend and then injection molded using a 200 ton Van Doren, 4 zone, 21/1 L/D, 8 ounce, 1 1/2" diameter general purpose screw having a 3 1/2 to 1 compression ratio operated at the conditions indicated  
15 below. A small pin gate (.032") was used. The mold produced flex bars (5" x 1/2" x 1/4").

### MASTER BATCH SAMPLE A

Contains - BASF Ultramid-B3 (Nylon 6) and color concentrate - White Pearl (Product #93,553CN) by Teknor Color Co. at 1% by weight.

20

Barrel Temperatures - Rear 350 - 410 - 400 - 390°F Nozzle

Mold Temperature - 70°F

1st Stage Pressure - 1600 psi

1st Stage Time - 10 seconds

25 2nd Stage Pressure - 1200 psi

2nd Stage Time - 5 seconds

Back Pressure - 40 psi

Screw RPM - 30

Shot Size - Maximum

30

From the samples produced for Sample A, it was critical with this sample to keep the melt temperature at 410 to 415°F. This material needs to be kept below the melt point of the Nylon-6 resin. Nylon-6 should not be well-mixed with Surlyn® PC-100 so as to not diminish the swirl effect within the part.  
35 The swirl effect is not on the surface, but it appears deeper inside of the part.

### MASTER BATCH SAMPLE B

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Contains - Selar® PA 3426 (Amorphous Nylon) and color concentrates - White Pearl (Product #93,553CN) by Teknor Color Co. at 1% by weight.

5    **MASTER BATCH SAMPLE C**

Contains - Selar® PA 3508 (Amorphous Nylon) and color concentrates - White Pearl (Product #93,553CN) by Teknor Color Co. at 1% by weight.

10   **Barrel Temperatures - Rear 320 - 330 - 330 - 330°F**  
**Nozzle**

**Mold Temperature - 70°F**

**1st Stage Pressure - 1600 psi**

**1st Stage Time - 10 seconds**

15   **2nd Stage Pressure - 1200 psi**

**2nd Stage Time - 5 seconds**

**Back Pressure - 50 psi**

**Screw RPM - 34**

**Shot Size - Maximum**

20

Both samples were processed with the same injection molding set up. Both samples had a whiter appearance than Sample A. Also there were more swirls on the surface of the part, which gives this material a totally different look.

25

**CLAIMS**

We claim:

1. A single injection process comprising first making a salt and pepper blend of a nylon/colorant master batch and an ionomer, then feeding the blend to a reciprocating screw injection machine having a single barrel, under conditions that maintain the nylon/colorant master batch in a state wherein it will flow but will have a viscosity greater than the ionomer so that it will not disperse well in the ionomer at the temperature of injection, the barrel feeding a nozzle which in turn feeds one or more sprues and, in turn, gates in the mold, the gates positioned so to impinge on the wall of the cavity or the core in the cavity.
2. A co-injection process comprising first feeding ionomer through a first barrel connected to a nozzle followed closely by feeding the nylon/colorant blend through a second barrel connected the same nozzle of a reciprocating screw injection machine operated under conditions that maintain the nylon/colorant master batch in a state wherein it will flow but will have a viscosity greater than the ionomer so that it will not disperse well in the ionomer at the temperature of injection, the barrels feeding a nozzle which in turn feeds one or more sprues and, in turn, gates in the mold, the gates are positioned so to impinge on the wall of the cavity or the core in the cavity.
3. The process of claim 1 or 2 wherein the nylon is an amorphous polyamide.
4. The process of claim 1 or 2 wherein the nylon is nylon 6 and the temperature is less than 205 °C.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/05630

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B29C45,16 //B29K77:00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 007, no. 145 (M-224), 24 June 1983 & JP 58 055234 A (SUMITOMO NAUGATUCK KK), 1 April 1983, see abstract	1-4
A	--- PATENT ABSTRACTS OF JAPAN vol. 009, no. 114 (M-380), 18 May 1985 & JP 60 000913 A (TAKIKIYO KK), 7 January 1985, see abstract	1-4
A	--- US 4 125 582 A (LANGLOIS JAMES L) 14 November 1978 see column 5, line 57 - column 6, line 4 --- -/--	1-4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

25 June 1997

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Attalla, G

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/05630

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 007, no. 209 (C-186), 14 September 1983 &amp; JP 58 108251 A (TORAY KK), 28 June 1983, see abstract -----</p>	1-4

Information on patent family members

PCT/US 97/05630

Form PCT/ISA/210 (patent family annex) (July 1992)

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